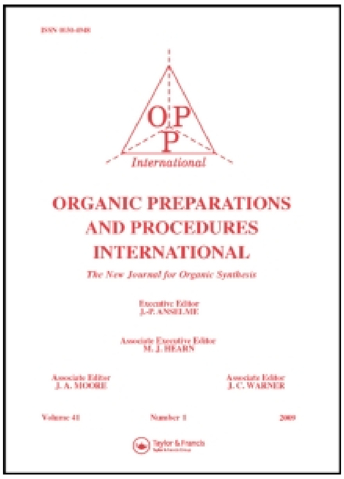

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AN EFFICIENT AND FACILE PROCEDURE FOR DEPROTECTION OF 1,1-DIACETATES USING ANHYDROUS FERROUS SULFATE

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The selective protection and deprotection of functional groups is of great importance in synthetic organic chemistry. 1,1-Diacetates have received increasing attention because these compounds are stable to oxidants,[1,2] readily prepared,[3-9] easily converted to the parent aldehydes and can serve as alternatives to acetals for selective protection of aldehydes.[10] They are also important starting materials for the synthesis of valuable intermediates of Diels-Alder reaction.[11,12] A literature search revealed that a number of methods have been reported for the conversion of 1,1-diacetates to corresponding aldehydes.[13] The following reagents have been used: alcoholic sulfuric[1] or hydrochloric[2] acid, either sodium hydroxide or potassium carbonate in aqueous THF,[3] boron triiodide-N,N-diethylaniline complex,[14] ceric ammonium nitrate (CAN) coated on silica gel in dichloromethane,[15] neutral alumina,[16] potassium phenoxides,[17] montmorillonite K-10 and KSF[18-20] and expensive graphite.[21] While each of the above methods has its own merit, some have drawbacks such as the need to use strong acids which other functional groups may not tolerate and long reaction time (no detailed results are given),[3] low yield (<66%),[14] and the use of microwave heating.[16,18,19]

Anhydrous ferrous sulfate has been used as a catalyst for organic reactions.[22-24] We previously developed an efficient procedure for preparation of 1,1-diacetates from aldehydes using a catalytic quantity of anhydrous ferrous sulfate.[22] Herein we report a rapid and efficient procedure for the deprotection of 1,1-diacetates catalyzed by anhydrous ferrous sulfate in refluxing dichloromethane, benzene or toluene.

$$\underset{\textbf{1}}{\mathrm{RCH(OAc)_2}} \xrightarrow[\Delta,\ \text{solvent}]{\mathrm{FeSO_4}} \underset{\textbf{2}\ (96\text{-}99\%)}{\mathrm{RCHO}} + \mathrm{Ac_2O}$$

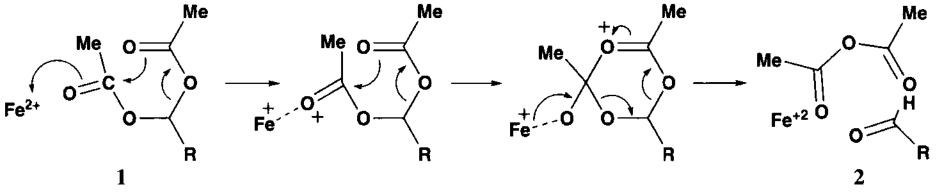
When solutions of 1,1-diacetates (**1**) in dichloromethane, benzene or toluene are heated at reflux in the presence of anhydrous ferrous sulfate, the corresponding aldehydes (**2**) are obtained in excellent yield (**Table 1**).

TABLE 1. Deprotection of 1,1-Diacetates in the Presence of Anhydrous Ferrous Sulfate

Entry	R	Solvent	Time (min)	Yield (%)[a]	mp.(°C) or bp.(°C)/Torr	Lit. mp.(°C) or bp.(°C)/Torr
a	C_6H_5	$C_6H_5CH_3$	10	98	60-62/10	179/751[25]
b	$4\text{-}CH_3C_6H_4$	CH_2Cl_2	15	99	104-106/10	204-205/760[25]
c	$4\text{-}CH_3OC_6H_4$	CH_2Cl_2	10	99	130-133/10	134-135/12[25]
d	$4\text{-}ClC_6H_4$	C_6H_6	20	98	46-47	47[25]
e	$3\text{-}ClC_6H_4$	C_6H_6	30	96	95-97/10	213-214/760[25]
f	$4\text{-}O_2NC_6H_4$	$C_6H_5CH_3$	10	98	105-107	106[25]
g	$3\text{-}O_2NC_6H_4$	$C_6H_5CH_3$	10	97	57-58	58[25]
h	$3,4\text{-}(OCH_2O)C_6H_3$	CH_2Cl_2	10	99	36-37	37[25]
i	$C_6H_5CH{=}CH$	CH_2Cl_2	15	98	128-13/20	130/20[25]
j	2-furyl	C_6H_6	15	98	53-55/10	162/760[25]
k	$CH_3(CH_2)_2$	C_6H_6	600	97[b]	75/760	75/760[25]
l	$CH_3(CH_2)_8$	$C_6H_5CH_3$	600	98[b]	85/10	208-209/760[25]
m	$CH_3(CH_2)_{16}$	$C_6H_5CH_3$	540	98[b]	38-40	38[25]

a) Isolated yield. b) Net yield, percent conversion of **1k** = 85%; percent conversion of **1l** = 80%; percent conversion of **1m** = 75%.

Mention must be made here that the conditions employed for the preparation of 1,1-diacetates with the aid of anhydrous ferrous sulfate are different from those used to effect cleavage. The formation of 1,1-diacetates under catalysis of anhydrous ferrous sulfate was carried out at room temperature, free of solvent in most cases and requires excess acetic anhydride (3 equiv.).[22] However, the rate of the cleavage reaction is markedly dependent on temperature. For example, complete conversion of phenylmethanediol diacetate (**1a**) and 3,4-methylenedioxyphenylmethanediol diacetate (**1h**) to the corresponding aldehydes (**2a** and **2h**) require 6 h in dichloromethane at room temperature. 4-Nitrophenylmethanediol diacetate (**1f**) and 3-nitrophenylmethanediol diacetate (**1g**) undergo 70% conversion after 2 h in refluxing benzene whereas 98% and 97% cleavage yields are obtained at the higher temperature of refluxing toluene. It is noteworthy that aliphatic 1,1-diacetates (**1k**, **1l** and **1m**) need longer reaction time and give lower per cent conversion.



Scheme 1

Proposed Mechanism for the Cleavage of 1,1-Diacetates in the Presence of $FeSO_4$

It is assumed that the reaction involves a unimolecular decomposition of the 1,1-diacetate to give an aldehyde and acetic anhydride. A hydroxamate test identified the presence of acetic anhydride in the reaction products. Furthermore, neither additional water nor the use of anhydrous conditions affect the reaction rate, implying that the reaction does not involve a hydrolysis.

In conclusion, we have provided a rapid, efficient and high yielding method for the deprotection of 1,1-diacetates which uses an inexpensive catalyst and does not require an aqueous workup.

EXPERIMENTAL SECTION

Anhydrous ferrous sulfate was obtained by heating $FeSO_4 \cdot 7H_2O$ at 190-200°/40 torr for 20 min. The organic products were characterized by ^1H NMR spectra and comparison of their melting or boiling points with authentic sample.

Preparation of 1,1-Diacetates.- A typical synthesis of phenylmethanediol diacetate (**1a**)[22] is briefly described here. A mixture of benzaldehyde (**2a**, 0.96 g, 10 mmol), acetic anhydride (3.06 g, 30 mmol) and anhydrous ferrous sulfate (200 mg) was stirred at room temperature for an hour. The catalyst was filtered off and washed with diethyl ether (2 x 10 mL). The filtrate was washed successively with 5% HCl (20 mL), 5% $NaHCO_3$ (20 mL) and brine (2 x 20 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give **1a** (1.94 g, 98%), mp. 45-46° (colorless cubics from cyclohexane), lit.[4] 44-46°.

General Procedure for the Deprotection of 1,1-Diacetates.- A mixture of 1,1-diacetates (**1**, 3.0 mmol), anhydrous ferrous sulfate (50 mg) and dichloromethane or benzene or toluene (5 mL) was stirred at refluxing temperature for the length of time indicated in Table 1. The reaction was monitored by TLC. After cooling of the reaction mixture, the catalyst was removed by filtration and washed with dichloromethane. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel (petroleum-dichloromethane as eluent) to give the corresponding aldehydes (**2**) in yields of 96-99% (**Table 1**).

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